Biogenic Emissions from Green Waste and Comparison to the Emissions Resulting from Composting Part II: Volatile Organic Compounds (VOCs)

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The cumulative emissions of volatile organic compounds (VOCs) resulting from natural decay of selected green waste, i.e. grass clippings, woodchips and prunings, and from composting of the same feedstock were studied. The results indicated that terpenes were the only compounds emitted from the feedstock as they underwent natural breakdown as well as during their composting. Even though there was a wide array of compounds emitted, the results suggested that the following six terpenes i.e., α -pinene, β -pinene, 3-carene, camphene, β -myrcene, and p-limonene, were the most significant compounds encompassing 32.7 to 95.3% of the total emissions. The cumulative VOC emissions varied considerably from a batch to another ranging 11.0 to 347.4 mg/kg-dw expressed as α -pinene. The composting of the same materials in different blends resulted in cumulative emissions ranging from 18.1 to 106.6 mg/kg-dw as α -pinene, representing 60 to 92% reduction compared to the biogenic emissions resulting from natural decay.

Introduction

With increases in human population and consumption of resources, communities all around the world are burdened by rapidly filling landfills. In response, regulatory agencies are challenged to maximize landfill space by instituting programs which emphasize waste reduction and recycling, and even impose regulations banning or limiting the disposal of certain waste streams into the landfills. Biodegradables make up the single largest portion of the municipal solid waste (MSW). It has been estimated that 40% of MSW generated in the state of California is biodegradable (Statewide Waste Characterization Study, Cascadia Consulting Group, Inc., December 2004). Therefore, biodegradables have been the foci of such programs and regulations. For instance, the City Council of Vancouver, British Columbia, passed a resolution to reduce the MSW by 50 percent (Henderson 1999). The Onondaga County, New York, Resource Recovery Agency banned disposal of grass, leaves, and prunings from the landfills in 1992 (LaLonde 2000). Similarly, AB 939 of California required all counties to divert 50 percent of MSW from landfills by the year 2000 (CIWMB 2005a).

Composting, while offering a viable alternative for the biodegradable waste streams with a value-added marketable end-product, is known to emit considerable amount of volatile and semivolatile compounds, collectively referred as VOCs, to the atmosphere. Depending on the feedstock being

processed and the operational conditions, a wide array of VOCs are being emitted. Yard waste composting primarily results in emissions of terpenes (i.e. the natural compounds released from the feedstock) and, to a lesser extent, alcohols, ketones and benzenes as a result of biological breakdown; while organic acids, alcohols and sulfides are the major compounds emitted from MSW composting (Eitzer 1995; Kim et al 1995 and Krzymien et al1999). VOCs are considered as major air pollutants due to their hazardous, malodorous and reactive properties. Of particular concern are the photochemical reactions taking place in the troposphere resulting in generation of secondary air pollutants including peroxyacetyl nitrates (PANs) and troposheric ozone (O₂), commonly referred as to the "brown" or "photochemical smog." With an increasing volume of materials being composted and more stringent air quality standards, a new wave of regulations, led by the South Coast Air Quality Management District (SCAQMD), are being imposed on composting facilities to reduce their emissions. SCAQMD, which is comprised of portions of Los Angeles, Riverside, and San Bernardino Counties, and all of Orange County, is a serious nonattainment area for particulate matter and extreme nonattainment area for ozone pollution. SCAQMD has already adopted three rules related to compostable materials. Rule 1133 is a rule that requires registration and general reporting from all chipping, grinding and composting facilities. Rule 1133.1 regulates grinding and chipping facilities, and

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Rule 1133.2 regulates cocomposting facilities. The SCAQMD is considering an additional rule, PR1133.3, to regulate green waste composting facilities (CI-WMB 2005b). While such regulations are aimed at improving the air quality, they disregard the fact that emissions from composting facilities are not necessarily of an anthropogenic source. Even though composting is a controlled process, the feedstock materials handled are the by-products of other activities such as agriculture and landscaping. Whether they are composted, disposed of into landfills, or managed otherwise, they will go through natural decay, still emitting compounds of biogenic source. For instance, a study conducted in Atlanta, Georgia concluded that up to 10% of the emissions in Atlanta were attributable to the biogenic sources (Lewis 1999). Furthermore, composting of organic matter is very likely to result in lower emissions than if they were handled otherwise. The VOCs emitted during the composting process, whether originated from the feedstock or resulted from the biological breakdown, are all natural compounds and amenable to biodegradation, except for rare contamination cases.

Composting will likely result in lower emissions because a properly managed composting matrix, i.e., a balanced C:N ratio, moisture content and aeration, provides microorganisms with an excellent environment resulting in an intense microbial activity. Biofilters utilizing compost have been used effectively for the treatment and removal of a variety of VOCs including those resulting from composting and even hard to biodegrade contaminants (Wani et al1998; Quinlan et al. 1999; Torkian et al. 2003). A literature review of use of biofilters for air pollution control is available elsewhere (Iranpour et al2005). Therefore, VOCs are very likely to be biodegraded within the composting matrix, and thus result in lower emissions when composted than if the materials were to be handled differently.

The goals of this study were to determine the biogenic VOC emissions resulting from natural decay of green waste, and to compare to those resulting from composting of the same materials to elucidate whether composting causes an increase or reduction of the emissions. The work presented here was part of a larger investigation, where ammonia emissions were also studied in a similar manner. The results of the ammonia investigation were published earlier (Chou and Büyüksönmez 2005).

Materials And Method

The green waste materials investigated in this study were prunings, woodchips and grass clippings.

Grass clippings were collected from the lawns of San Diego State University on the day of the experiments. Woodchips and prunings were obtained from the Miramar Composting Facility operated by the City of San Diego. Freshly ground prunings were collected from the grinder on the day of the experiments; while woodchips were taken from a pile that was sitting for an unknown duration.

The feedstock materials were dried at 70°C, ground and analyzed for composting related characteristics — carbon, nitrogen, moisture and ash contents and pH. The carbon content was determined with a Shimadzu TOC-500 total organic carbon analyzer equipped with a SSM-5000A solid sample module using a glucose calibration with approximately a 30 mg sample. The Kjeldahl method, as described in "Test Methods for the Examination of Composting and Compost" (TMECC), was followed to digest samples for nitrogen determination. The digested solution was cooled down and combined with 10 ml of deionized water. The solution was distilled after combining with 20 ml of 10 N NaOH. The distillate was collected in an indicating solution of 33 M boric acid containing methyl red and blue. The solution was titrated with 0.02N H₂SO₄ to determine the total nitrogen. The moisture and ash contents were determined gravimetrically after drying at 105°C and igniting at 550°C, respectively. The pH of the samples was determined by saturated paste method.

Biogenic Modeling Setup and VOC Emissions

The experimental setup shown in Figure 1 was used to collect the biogenic VOC emissions resulting from the natural decay of the material. The experimental setup included a set of flux chambers made from polycarbonate with air inlets and a perforated

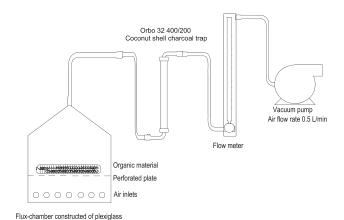


FIGURE 1. Schematic of the flux chamber and sampling train setup for determination of biogenic VOC emissions.

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aluminum retaining shelf, coconut shell charcoal organic traps (Orbo 32® 400/200, Supelco), a rotameter and a vacuum pump. A known amount of material was placed on the retaining shelf and air was drawn through the organic trap at a rate of 500 ml/min. At timed intervals, the organic traps were replaced, extracted with solvent and analyzed with a gas chromatography-mass spectrometer (GCMS) as described in Analytical Method section.

Composting Simulation Setup And VOC Emissions

In order to compare the biogenic VOC emissions to those resulting from composting, blends of feed-stock were composted in a bench scale self-heating composting simulation setup for up to 42 days. The setup was comprised of six-gallon air-tight, stainless steel reactors that are housed in polyurethane foam insulated bins as described in Figure 2. Compressed air was passed through an activated carbon filter to remove possible contaminants and then bubbled through a water column to prevent excessive moisture loss during the course of the experiment. The treated air was introduced from the bottom of the reactor with a perforated copper coil. Two inches of gravel and a perforated aluminum plate were placed above the aeration coil.

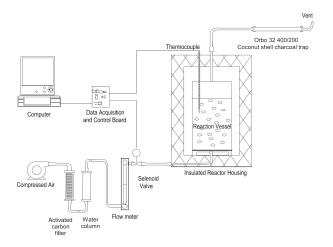


FIGURE 2. Schematic of the bench-scale composting simulation reactor setup

The feedstock was blended with a concrete mixer at different C:N ratios and moisture contents and then loaded into the reactors. Reactors were opened at weekly intervals to remix and add water, if needed, to bring it back to the initial moisture content. The effluent air was passed through organic traps. The temperatures of the reactors were collected with a thermocouple probe inserted to the center of the

reactors and logged to a personal computer through a Daisy Lab data acquisition system.

Analytical Method

The analytical method used in this study was based on a protocol that was described by Komilis and Ham (2000) and Komilis et al. (2004). The contents of the adsorption tubes (Orbo 32® 400/200) were emptied into glass vials and combined with 4-ml of carbon disulfide and shaken for 30 minutes with a wrist-action shaker. The vials were then centrifuged for 5 minutes. A 1-ml sample of the extract was transferred into an amber auto-sampler vial and spiked with 2 μl of 2μg/μl 4,4'-dibromooctafluorobiphenyl solution in methanol as the internal standard. Extracts were analyzed with a Hewlett Packard (HP) 6980 gas chromatograph and a HP 5973 mass spectrometer (GC-MS) equipped with a 30 m x 0.25 mm fused silica Valcobond VB-5 column. The inlet and MS temperatures were maintained at 150°C and 300°C, respectively. Helium was used as the carrier gas at a column flow rate of 1 ml/min, and a sample was injected with a split ratio of 1:50. The column temperature was initially maintained at 40°C for two minutes and ramped up to 250°C at a rate of 10°C/min. After holding at 250°C for 14 minutes, the temperature was raised to 290°C to condition the column for the subsequent run.

The peak areas were normalized with respect to the internal standard peak area. The total terpene emissions are reported as the total normalized peak areas excluding the areas of internal standard and carbon disulfide, if present. Even though the method was evaluated by Komilis and Ham (2000), adsorption and extraction efficiency of the adsorption traps were determined for a set of terpenes prior to beginning of the study. The efficiencies were higher than 77% for all chemicals tested except for α –terpinene, which was determined to be 48.2% It should be noted that α –terpinene was not present in actual samples; thus the low analytical efficiency for α –terpinene was not a concern. The list of chemicals and the corresponding efficiencies are presented in Table 1.

TABLE 1.
Trapping and extraction efficiencies for select terpenes

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Compound Efficiency, %		Compound	Efficiency, %
Camphene	89.2	Myrcene	91.4
3-Carene	79.1	α-Pinene	98.9
Eucalyptol	83.3	β-Pinene	88.1
Limonene	77.2	α–Terpinene	48.2

Results And Discussion

Biogenic VOC Emissions

The biogenic VOC emissions were determined qualitatively and quantitatively for grass clippings, woodchips and prunings for up to 220 days for materials listed in Table 2 with selected characteristics. Grass clippings were obtained from the same location directly following the mowing. Since no significant variation between the batches was anticipated, emissions from grass clippings were determined for only one batch. However, due to very high variability expectations, emissions from woodchips and prunings were determined for 2 and 3 separate batches, respectively.

TABLE 2. Selected characteristics of feedstock materials tested in flux chambers for determination of biogenic VOC emissions

Raw Material Mass	Loading kg)	Moisture (%)	Dry Mass (kg)	C (%)	N (%)	C/N Ratio	Ash (%)	рН
Grass	0.074	70.63	0.02	45.0	4.0	11.3	8.8	6.3
Wood Chips-I	0.352	9.23	0.38	43.0	0.4	107.5	1.0	4.9
Wood Chips-II	0.43	34.79	0.31	49.1	0.5	98.2	2.7	4.8
Prunings-I	0.414	24.87	0.26	43.4	1.7	25.5	20.6	6.4
Prunings-II	0.468	45.03	0.24	47.9	1.3	36.9	7.7	6.3
Prunings-III	0.506	48.61	0.26	38.8	0.9	43.1	25.7	6.6

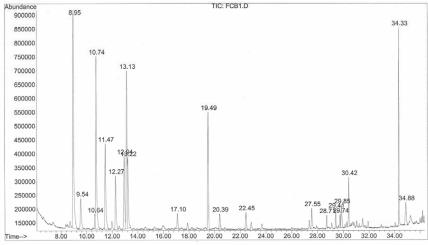


FIGURE 3. Sample chromatograph from biogenic grass emissions

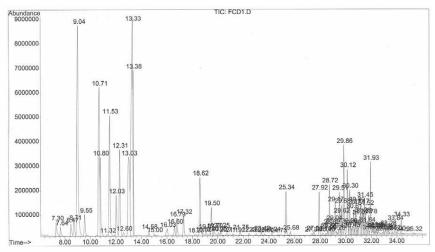


FIGURE 4. Sample chromatograph from biogenic woodchips (batch 1) emissions

The results show that terpenes were the single most important type of compounds emitted from the feedstock tested in this study. The sample chromatographs are presented in Figures 3 through 7 (the elution times are listed in Table 4). Even though there was a wide array of compounds emitted, the results suggested that the following six terpenes i.e., α-pinene, β-pinene, 3-Carene, camphene, β-myrcene, and -limonene, were the most significant compounds encompassing 32.7 to 95.3% of the total emissions. Therefore, only these compounds were determined quantitatively as presented in Table 3 along with the percentage make ups in the total emissions. α-Pinene was the most prevalent compound representing either the largest or the major portion of the total emissions for all materials tested. It represented the 10.2% of the emissions from grass clippings, secondary to β-myrcene; and made up the largest portion of the emissions from woodchips accounting 44.1 and 72.7% of the total emissions for two separate batches. For prunings, α-pinene concentration was either the largest or secondary to D-limonene. Even though their concentrations were not determined, the following compounds were identified in emissions: ocymene, eucalyptol and humulene from grass clippings; α-phellandrene, o-cymene, terpineol, estragol, caryophyllene from woodchips; and α-phellandrene, eucalyptol, thujone, camphor, borneol and β-quaiene from prunings. All of the compounds identified in this study belong to a major class of natural VOCs called terpenes. Komilis et al. (2004) studied the VOC emissions from MSW and yard waste; and reported that terpenes were the major class of VOCs emitted from the yard waste composting. The molecular structures, formulas and the retention times (for Figures 3-7) of the most prevalent terpenes are presented in Table 4. The internal standard's retention time was 34.3 min.

The composition of the VOCs emitted from two batches of woodchips did not show a large variation even though the level of emission was substantially lower for the second set. The woodchips originated from recycled construction wood and used pallets, which are typically made from Douglas fur or Pine lumber. Therefore, the similarity in composition of emissions was expected. The large difference in the amounts of VOCs emitted was at-

tributed to the weathering and the age of the wood. Unlike woodchips, the composition of the emissions from prunings varied considerably between the batches, while the amount of VOCs emitted had a lower variability compared to woodchips. Even though prunings were obtained freshly at the grinder, the type of tree and/or shrub ground varied by the minute. The differences in smell and odor intensity were noticeable by nose at the time of collection. These factors could have accounted for the composition variability of the pruning emissions.

In order to simplify the comparisons and total emissions determinations, two approaches were followed. The first approach used the sum of the six indicator terpenes as a means of estimating total VOC emissions as calculated by the equation below to account for compounds that were not quantitatively determined as shown in Equation 1.

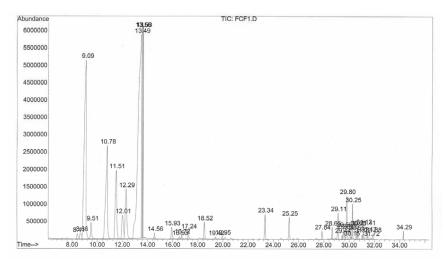


FIGURE 5. Sample chromatograph from biogenic woodchips (batch 2) emissions

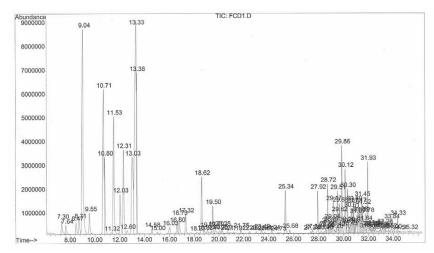


FIGURE 6. Sample chromatograph from biogenic prunings (batch 1) emissions

Total VOC Emissions
$$(mg/kg - dry) = 100 (\%) \dots (1)$$

$$\left(\frac{Sum \text{ of 6 Indicator Terpenes } (mg/kg - dry)}{Sum \text{ of 6 Indicator Terpenes } (\% \text{ of Total Area})}\right)$$

After comparing the emissions results, it became apparent the α -pinene compound by itself provided a fairly good approximation of total VOC emissions. Therefore, evaluating emissions using the single indicator, α -pinene, became the second approach. In this approach, the total peak areas except the internal standard were reported as α -pinene. In fact, VOC concentrations as determined solely by α -pinene, i.e., treating the sum of the response areas as α -pinene, only differed by an average of 7.4 % when compared to those values determined from the concentrations of the six indicator terpenes (Table 5). Therefore, cumulative VOC emissions resulting from biogenic decay of materials and during composting were determined in

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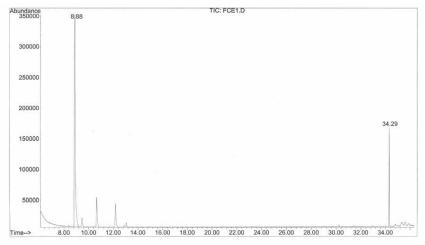


FIGURE 7. Sample chromatograph from biogenic prunings (batch 2) emissions

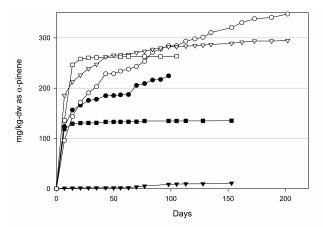


FIGURE 8. Cumulative VOC emissions resulting from biogenic decay expressed as α-pinene: ● - grass; ○ - woodchips-I; ▼ woodchips-II; ∇- prunings-I; - prunings-II: - prunings-III

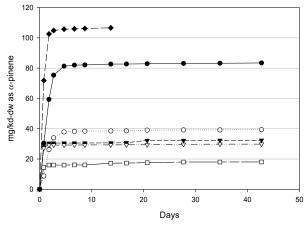


FIGURE 9. Cumulative VOC emissions resulting from composting of feedstock expressed as α-pinene: ● - Run#1 (initial C/N: 27.2 & MC 65%); ○ - Run#2 (initial C/N: 47.2 & MC 56%); ▼ - Run#3 (initial C/N: 48.5 & MC 56%); ∇- Run#4 (initial C/N: 21 & MC 54%); ■ - Run#5 (initial C/N: 21.5 & MC 63%); □ - Run#6 (initial C/N: 20.3 & MC 77%; ♦ - Run#7 (initial C/N: 18.4 & MC 55%).

terms of α -pinene concentrations.

The cumulative VOC emissions, determined as α-pinene concentration, are presented in Figure 8. These experiments continued from 99 days to 202 days depending on the availability of flux chambers, the current level of emissions, and the start up of the composting experiments. The results show that most of the VOCs were emitted within the first two weeks for grass clippings and prunings. On the other hand, woodchips continued to emit VOCs for longer period times; when the experiments stopped, they were still emitting VOCs. It should be noted that the emissions, later in the

experiments, had fallen below the emissions of the control flux chamber (i.e. the background VOCs). Considering the fact that woodchips and prunings are common biofilter media, this was attributed to the biofilter effect of the test material.

Comparison of Biogenic Emissions To Composting Emissions

In order to determine the VOC emissions resulting from composting of the same feedstock, materials were blended together in different proportions and moisture contents and composted up to 42 days in the lab-scale composting reactors. The C:N ratio varied from 19.4:1 to 48.5:1 and the moisture content ranged from 55 to 77% as presented in Table 6.

The cumulative VOC emissions resulting from composting experiments are presented in Figure 9. The composting of the blends (Run 1 through 6) resulted in emissions ranging from 18.1 to 83.5 mg VOC as α -pinene/kg-dw of blend; it should be noted that the emissions from composting runs were in the order of 20-40 mg/kg except for the first run. When prunings were composted as received, i.e. without blending with other feedstock and addition of moisture (Run 7), it resulted in a cumulative VOC emission of 106.6 mg/kg-dw. Figure 10 presents the comparison of the measured emissions resulting from composting to the calculated biogenic emissions if materials that went into the blends were left to undergo natural decay based on their actual weights in the blend. The comparisons were made using the emissions results up to the 42nd day (14 days for the 3rd batch of prunings), which is how long the composting experiments were continued, and using the final biogenic emissions results for

TABLE 3.

Composition of the emissions from selected green waste feedstock

Grass clippings α-Pinene	Material	Compound	Retention Time Minimum	Concentration mg/ kg-dw	Percent Fraction to Total Emissions
β-Myrcene 11.45 15.24 11.11 3-Carene 12.29 11.42 2.54 D-Limonene 13.02 14.08 6.26 Total 69.50 32.74 Wood -1 α-Pinene 153.03 44.05 Camphene 3.44 0.99 β-Pinene 49.40 15.80 β-Myrcene 4.69 2.24 3-Carene 77.70 11.18 D-Limonene 38.47 11.07 Total 326.93 85.34 Wood -2 α-Pinene 10.12 72.68 Camphene 0.28 2.03 β-Pinene 1.24 9.90 β-Myrcene 0.02 0.00 3-Carene 2.59 9.33 D-Limonene 0.14 0.99 Total 14.39 95.26 Prunings -1 α-Pinene 36.42 12.36 Camphene 2.29 0.78 β-Pinene 20.04 7.56 β-Myrcene 36.47 12.38 β-Myrcene 36.47 12.38 Total 113.69 37.23 Prunings -2 α-Pinene 22.17 16.40 Camphene 1.72 1.27 β-Pinene 9.39 7.72 β-Myrcene 3.88 4.75 3-Carene 11.07 4.10 D-Limonene 58.49 43.28 Total 106.72 77.52 Prunings -3 α-Pinene 98.68 37.42 Camphene 4.86 1.84 β-Pinene 28.18 11.88 β-Myrcene 3.55 4.39 D-Limonene 23.15 4.39 D-Limonene 7.50 4.72 3-Carene 21.58 8.18 1.180 1.110 2.158 8.18 1.110 1.120 2.158 8.18 1.110 1.120 2.158 8.18 1.110 1.120 2.158 1.120 2.15	Grass clippings				
3-Carene 12.29 11.42 2.54 D-Limonene 13.02 14.08 6.26 Total 69.50 32.74 Wood - 1 α-Pinene 153.03 44.05 Camphene 3.44 0.99 β-Pinene 49.40 15.80 β-Myrcene 4.69 2.24 3-Carene 77.70 11.18 D-Limonene 38.47 11.07 Total 326.93 85.34 Wood - 2 α-Pinene 1.24 9.90 β-Pinene 9.28 2.03 β-Pinene 9.28 2.03 β-Pinene 1.24 9.90 β-Myrcene 3.02 0.00 3-Carene 2.59 9.33 D-Limonene 0.14 0.99 Total 14.39 95.26 Prunings - 1 α-Pinene 2.04 7.56 β-Myrcene 3.642 12.36 Camphene 2.29 0.78 β-Pinene 2.04 7.56 β-Myrcene 3.647 12.38 Total 113.69 37.23 Prunings - 2 α-Pinene 3.647 12.38 Total 113.69 37.23 Prunings - 2 α-Pinene 9.39 7.72 β-Myrcene 3.88 4.75 3-Carene 11.07 4.10 D-Limonene 58.49 43.28 Total 106.72 77.52 Prunings - 3 α-Pinene 9.8.68 37.42 Camphene 4.86 1.84 β-Pinene 9.8.68 37.42 Camphene 4.86 1.84 β-Pinene 28.18 11.88 β-Myrcene 3.15 4.39 D-Limonene 7.50 4.72 3-Carene 23.15 4.39 D-Limonene 7.50 4.72 3-Carene 23.15 4.39 D-Limonene 7.50 4.72 3-Carene 23.15 4.39 D-Limonene 7.50 4.72 3-Limonene 23.15 4.39 D-Limonene 21.58 8.18		β-Pinene	10.72	0.89	0.42
Data Total 13.02 14.08 6.26 Total 69.50 32.74		β-Myrcene	11.45	15.24	11.11
Total 69.50 32.74 Wood - 1 α-Pinene 153.03 44.05 Camphene 3.44 0.99 β-Pinene 49.40 15.80 β-Myrcene 4.69 2.24 3-Carene 77.70 11.18 D-Limonene 38.47 11.07 Total 326.93 85.34 Wood - 2 α-Pinene 10.12 72.68 Camphene 0.28 2.03 β-Pinene 1.24 9.90 β-Myrcene 2.59 9.33 D-Limonene 0.14 0.99 Total 14.39 95.26 Prunings - 1 α-Pinene 20.04 7.56 β-Myrcene 36.42 12.36 Camphene 2.29 0.78 β-Pinene 20.04 7.56 β-Myrcene 36.47 12.38 Total 113.69 37.23 Prunings - 2 α-Pinene 22.17 16.40 Camphene 1.72 1.27 β-Pinene 9.39 7.72 β-Myrcene 3.88 4.75 3-Carene 11.07 4.10 Camphene 58.49 43.28 Total 106.72 77.52 Prunings - 3 α-Pinene 98.68 37.42 Camphene 4.86 1.84 β-Pinene 98.68 37.42 Camphene 4.86 1.84 β-Pinene 9.39 7.50 4.72 3-Carene 23.15 4.39 D-Limonene 7.50 4.72		3-Carene	12.29	11.42	2.54
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_D -Limonene 21.58 8.18					
Total 183.95 68.44		D		21.50	0.10
		Total		183.95	68.44

the given set of materials. This comparison shows that composting results in substantially lower emissions than biogenic emissions, i.e. the emissions if the materials were left alone and allowed to undergo natural decay. The reductions in VOC emissions through composting ranged from 60 to 88% for

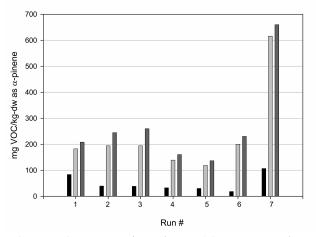


FIGURE 10. Comparison of cumulative VOC emissions resulting from calculated biogenic decay* versus composting: ■ - emissions from composting of blends for 42 days; ■ - biogenic emissions for 42 days; ■ - long term biogenic emissions (*calculated based on the proportions of the feedstock in the composting blend)

blends; and it was 92% for the prunings alone. Since many facilities compost the yard waste as it is received without blending with other feedstock, therefore it can be said that composting facilities handling yard waste, in fact, help lower VOC emissions. This reduction is attributed to the biodegradation of the VOCs as a result of intensified microbial activity during composing that is absent when the material is left undergo natural decay.

The earlier studies about the use of biofilters for air pollution control reported up to 100 percent removal efficiencies for many pollutants including hard-to-biodegrade toxic contaminants. Quinlan et al. (1999) obtained up to 99% removal efficiency for mixture of benzene, toluene, ethylbenzene and xylenes (BTEX). Ergas et al. (1995) obtained more than 97 percent removal efficiency for trichloroethylene (TCE). A literature review paper was published by Iranpour et al. (2005) for the use of biofilters for air pollution control. Giggey et al. (1994) (after Iranpour et al. 2005) studied the removal of three terpenes — α -pinene, β -pinene and β limonene, which were determined to be the most significant VOCs emitted from green waste in this study, and reported removal efficiencies of 100% for pinenes and 97% for p-limonene. Furthermore, as a part of this study, ammonia emissions were also investigated in the same manner described here (Chou and Büyüksönmez 2006). The results of this study also showed substantial reductions of ammonia emissions by composting the feedstock. Therefore, the composting process and facilities should be viewed as a means of lowering the emissions, rather than being looked at as the emission source.

TABLE 4. Molecular structures and formulas terpenes identified in this study

Compound	MW g/mole	Formula	Retention Time, Min.*	Structure	Compound	MW g/mole	Formula	Retention Time, Min.*	Structure
Borneol	154.25	C ₁₀ H ₁₈ O	13.3	HO	Humulene	204.35	C ₁₅ H ₂₄	30.4	\(\hat{\partial}\)
Camphene	136.23	$C_{10}^{}H_{16}^{}$	9.5	本	_D -Limonene	136.23	$C_{10}H_{16}$	13.1	$\!$
Camphor	152.23	C ₁₀ H ₁₆ O	16.6	X	β-Myrcene	136.23	$C_{10}H_{16}$	11.5	
3-Carene	136.23	$C_{10}^{}H_{16}^{}$	12.3	$\bigvee\!$	α-Phellandrene	136.23	$C_{10}H_{16}$	12.0	$\rightarrow \bigcirc$
Caryophyllene	204.35	$C_{25}^{}H_{24}^{}$	29.8	07	α-Pinene	136.23	$C_{10}H_{16}$	9.0	XX.
o-Cymene	134.22	$C_{10}^{}H_{14}^{}$	13.0		β-Pinene	136.23	$C_{10}H_{16}$	10.7	A
Estragol	148.20	$C_{10}^{}H_{12}^{}O$	21.3		Terpineol	154.25	$C_{10}^{}H_{18}^{}O$	21.0	но
Eucalyptol	154.25	C ₁₀ H ₁₈ O	12.2	√ ₀ → ⟨	Thujone	152.23	$C_{10}H_{16}O$	17.3	$\succ \!$

^{*}Retention times may vary ± 0.2 minute.

TABLE 5. Cumulative biogenic VOC emissions from feedstock

Material	6 Indicator Terpenes	AsPinene	Difference	Difference	
	(mg/kg-dry)	(mg/kg-dry)	(mg/kg-dry)	(%)	
Grass-1	212.30	224.59	12.29	5.79	
Wood-1	382.87	347.39	35.49	9.27	
Wood-2	15.11	11.03	4.07	26.97	
Prunings-1	305.40	294.67	10.73	3.51	
Prunings-2	137.67	135.13	2.53	1.84	
Prunings-3	268.78	263.66	5.12	1.91	
Average Difference				7.42	

TABLE 6. Selected characteristics of composting blends

Run	#1	#2	#3	#4	#5	#6	#7
Total weight (kg)	4.1	4.5	5.0	3.0	4.4	7.6	5.6
Total weight (kg-dw)	1.4	2.0	2.1	1.4	1.6	1.8	2.5
Grass (kg-dw)	0.31	0.23	0.15	0.39	0.46	0.5	_
Wood Chips (kg-dw)	0.43	1.07	1.45	0.33	0.39	0.43	_
Prunings (kg-dw)	0.78	0.58	0.38	0.56	0.66	0.72	2.5
Moisture (%)	65	56	56	54	63	77	55
рН	6.4	6.3	5.9	5.8	6.0	6.1	6.0
C/N Ratio	27.2	47.2	48.5	21	21.5	20.3	19.4
Ash (%)	18.8	4.8	2.0	10.8	9.4	16.4	25.7

Conclusion

The results of this study show that grass clippings, woodchips and prunings emit a variety terpene type of VOCs to the atmosphere. The study results show that

the majority of the emissions are due to the volatilization of natural compounds that are in the material, and not from biological metabolism. α -Pinene, β -pinene, 3carene, $\beta\text{-myrcene},$ and $_D\text{-limonene}$ were identified as the most significant VOCs emitted. The level of emissions from woodchips varied substantially, while the compositions of VOCs were similar. For prunings, on the other hand, the composition showed a large variation while the emission levels did not vary to the extent of VOCs from woodchips. Composting of the same materials has resulted in substantially lower emissions than the emissions that occur from natural biodegradation of the same types of materials.

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